

Materials Corrosion and Mitigation Strategies for APT:
Using Solution Resistivity as an Estimate of Tungsten Corrosion
in Spallation Neutron Target Cooling Loops

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Executive Summary

During the period 7/96-10/96, we monitored the water conductivity and chemistry of the materials irradiation flow loop in the A6 target station. This system is a closed loop which contains a number of tungsten rod bundles which serve as the neutron spallation source for the A6 experiments. Upon irradiation of a freshly purged system, we observed a consistent decrease in the water resistivity with increasing beam current and irradiation time. For this system it was demonstrated (via ICP concentration analysis) that this decrease in resistivity may be attributed solely to the dissolution of tungsten ions from the tungsten irradiation specimens. By calculating the rate of dissolution from these resistivity data, it was shown that the corrosion rate of tungsten can be determined. From these results it was concluded that solution resistivity measurements alone may be used to estimate corrosion rates of tungsten neutron spallation targets.

It may also be noted that the corrosion rates measured in this work (from both ICP solution analysis and resistivity measurements) are undesirably high, suggesting that a corrosion mitigation strategy is essential to the successful operation of the future APT accelerator if unclad tungsten is to be used as the target material.

Introduction

To examine the effects of radiation on candidate materials for the APT Target / Blanket system, a multi faceted approach has been employed. The focus of these efforts has been on the fabrication of a corrosion test loop to be placed at the LANSCE A6 Target Station[1]. This test loop will allow us to measure real-time corrosion of candidate materials being directly irradiated by a 1 mA, 800 MeV proton beam as well as examine corrosion mitigation strategies. To compliment these experiments, the tungsten closed water loop (currently being irradiated at the LANSCE A6 target station) was instrumented with a conductivity probe and water sampling line. The installation of these two diagnostic tools allowed us rudimentary evaluation of the severity of corrosion in the test loop. This report documents our semi-quantitative assessment of the corrosion rate of the tungsten target material.

Experimental

The tungsten insert used in these experiments was located at the LANSCE A6 Target Station (LANL). It was constructed in August 1996 and began a 2 month irradiation period at the end of August, 1996. This radiation period ended in late October of that year. The insert was constructed primarily from stainless steel 304L although it did contain some type-K thermocouples mounted in place by Ag-Zn brazes. The insert served to cool 10 tungsten rod-bundle assemblies which consisted of 19 1/8"-diameter W rods measuring 6" in length (rod bundle area: 450 in², 2.89x10³ cm²). In addition there are 2 W ring-bundle assemblies with sum area of 34.7 in² (223.9 cm²). The total surface area of W exposed to the cooling water is then 485 in² (3.11x10³ cm²). The rods (in the rod-bundle assembly) were welded onto SS 304L mounting fixtures which were then e-beam welded into 0.65" ID tubes. These tubes were conduits for the cooling water. A similar procedure was followed for the ring-bundle assembly. The cooling water (approximately 65 gallons) was deionized and replaced (with a flushing procedure to remove any residual impurities) prior to each measurement. The insert was aligned such that the W rod

bundles were centered with the beam center line. The proton beam had an energy of 800 MeV and an average current of approximately 1 mA. The spot size measured approximately 3 cm in diameter and was Gaussian in nature.

During the irradiation, solution resistivity measurements were carried out during three separate measurement periods: September 13-19, October 15-16, and the final October 30-31. Resistivity measurements were conducted with a three electrode probe (constructed from Hastelloy C276) specially designed and calibrated for this purpose [1,2]. Prior to each of these tests, the beam was turned off. Following a cool down period (approximately 1 hour) the entire cooling system was drained, flushed, and refilled with deionized water after which the beam was turned back on. During the measurement period no intentional bleed or drain of the system water was employed except where noted. Cooling water samples were taken concurrently with the solution resistivity measurements. These samples were analyzed for metal impurities (i.e., Fe, Ni, Cr, W etc...) by Inductively Coupled Plasma (ICP) and Gamma Spectrum Analysis.

Results and Discussion

Solution Resistivity Measurements Results of the initial solution resistivity measurements (Sept. 13-19) are presented in Figure 1. As shown in this figure, a large drop in the solution resistivity (from 7×10^5 to 3×10^4 ohm cm) was observed in the first 12 hours after the beam was turned on to 1 mA. After this initial drop, the solution resistivity decayed linearly. The final value measured on 9/19 was approximately 5×10^3 ohm cm. After this period, the water system was simultaneously bled and refilled with deionized water at a rate of approximately 24 gallons per hour.

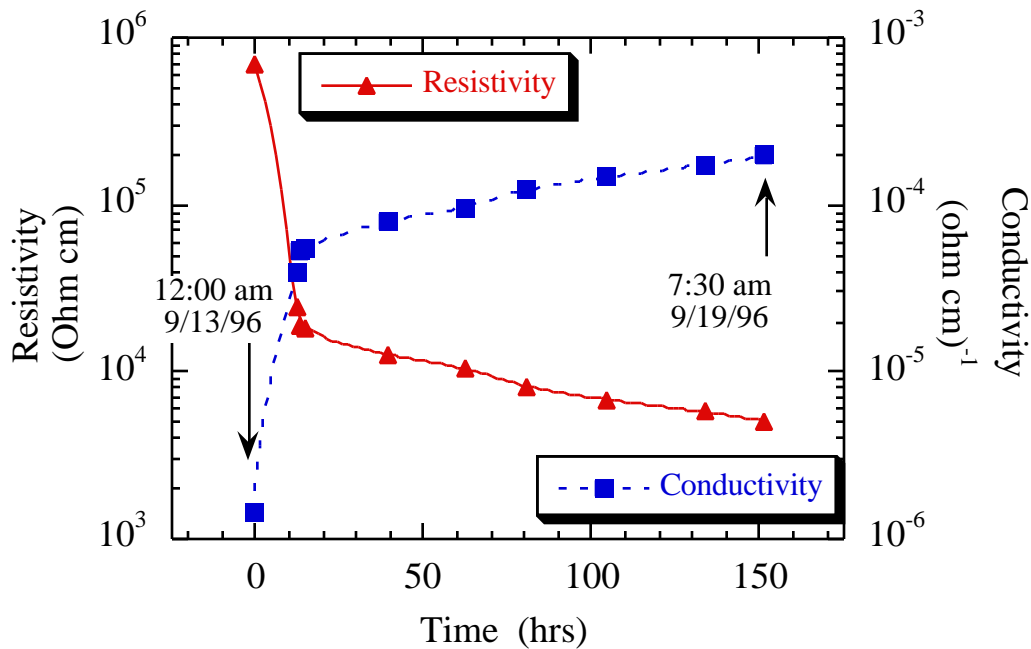


Figure 1 Initial solution resistivity measurements (ρ) on the tungsten cooling water loop. Experiments were conducted between September 13 - 19. Data is also presented as conductivity ($\sigma=1/\rho$) on the right axis.

The effects of beam current and time on solution resistivity were more closely examined on October 15-16. Prior to this experiment, the water system was flushed and refilled with deionized water. As shown in Figure 2a, a large drop in the solution resistivity from its initial value of 2×10^6 to a value of 5×10^5 ohm cm was observed after the beam was turned on. Over the next 20 minutes, the proton beam current was increased from 0.2 to 1 mA. During this time the solution resistivity decreased to approximately 4×10^5 ohm cm. The beam current was maintained at 1.0 mA for the remainder of the experiment. During the next 200 minutes (3.3 hrs) the solution resistivity fell exponentially to 7×10^4 ohm cm. After this exponential drop, the solution resistivity fell linearly during the next 600 minutes (10 hrs) to a value of 2×10^4 ohm cm (Figure 2b).

The effects of flushing the cooling water system were examined at the end of this measurement period (on 9/19/96). During the time which the system was bled (approximately 1/2 hours) resistivity measurements were made. As presented in Figure 3 a small increase in the

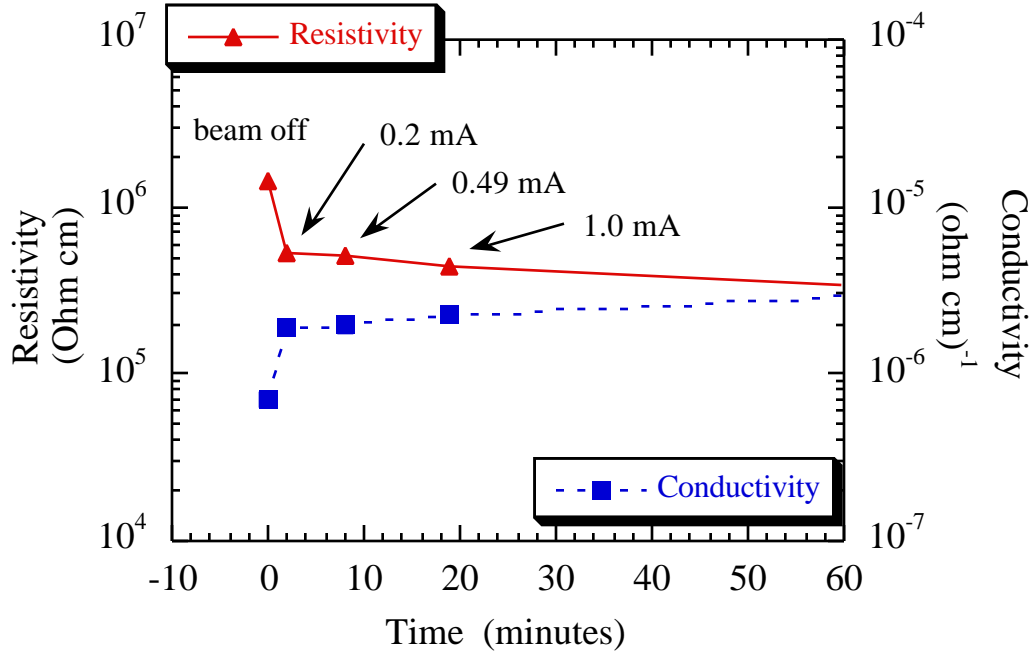


Figure 2a Solution resistivity as a function of beam current and time of exposure during the Oct 15-16 measurement period. While a fairly large change in solution resistivity was observed between the beam off and beam on measurements, a relatively small change was observed upon ramping the current from its initial value of 0.2 Ma to its final value of 1.0 mA.

solution resistivity was noted during this time. Unfortunately, to limit emissions from the radioactive water, only 12 gallons of the approximate 60 total were flushed from the system.

It is possible to use these ICP concentration measurements to calculate a theoretical solution resistivity as a function of beam current and time of irradiation. Recall that solution resistivity (ρ) is proportional to the concentration of impurities:

$$\rho = \frac{1}{\sum_i \lambda_i c_i} \quad \text{Eq. 1}$$

where λ is equivalent conductance and c is concentration. Therefore, while the initial changes in solution resistivity are exponential they are associated with far smaller corrosion rates of the target material (which result in dissolved W^{+6} in solution). At longer beam times the linear changes

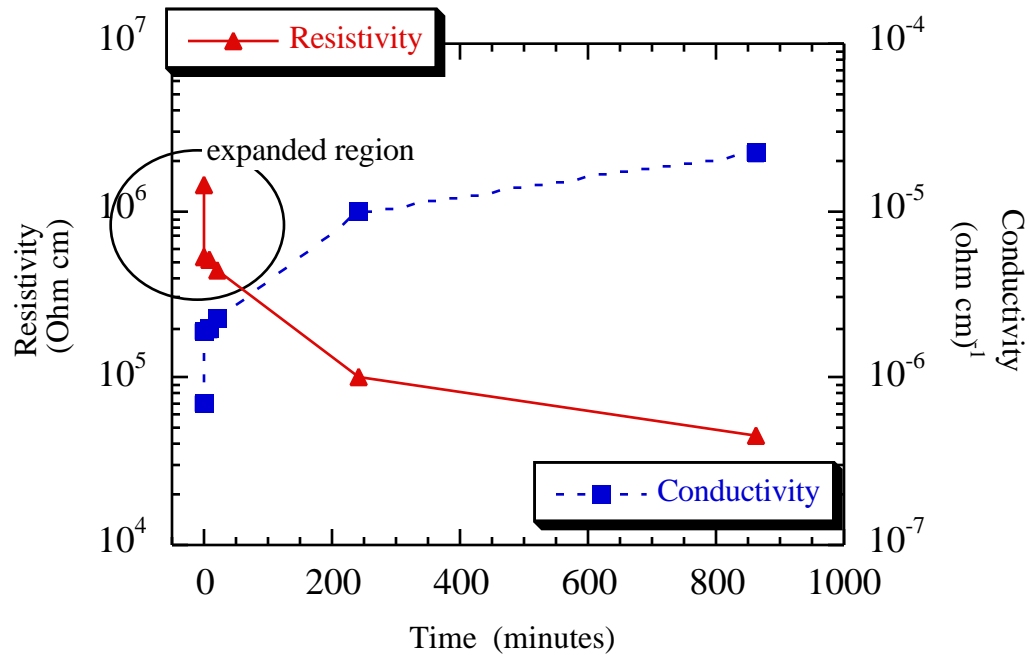


Figure 2b Solution resistivity as a function of beam current during the Oct 15-16 measurement period. The expanded region is shown above in Figure 2a.

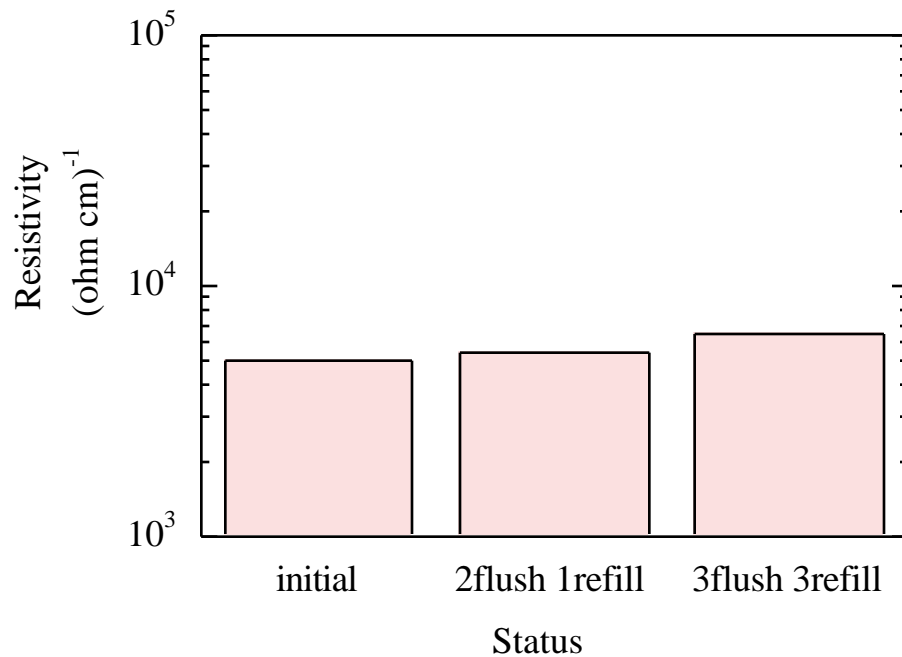


Figure 3 Effects of flushing water from the tungsten cooling water loop on solution resistivity. “1flush” refers to dumping 4 gallons of water from the 65 gallon system. “1refill” refers to replacing all of the 4 gallons of water dumped from the system. The “initial” measurement coincides with the final measurement in on Oct 16 (Figure 2b, 875 minutes).

observed are associated with much higher corrosion rates of the target material (Figure 1). As discussed later, this assumes that the observed changes in resistivity owe to a change in concentration of tungsten in solution and not to other species.

During the final measurement period, Oct. 30-31, solution resistivity measurements and cooling water sampling were made concurrently. As before, prior to this experiment, the water system was flushed and refilled with deionized water. Water samples were analyzed by ICP for total dissolved solids and by Gamma Spectral Analysis for radio-isotopes. The results are presented in Table 1. As presented in this table, the same decrease in solution resistivity observed in Figures 1-3 were observed during this period. ICP found no measurable concentration of Fe, Ni, Cr, or Mo in the system, an indication that no appreciable corrosion of the plumbing system was occurring during the test period. However, large concentrations of W were found in the water samples as shown in Table 1. The theoretical solution resistivity which would arise from the measured W concentrations have been calculated from Equation 1. These calculations assume the value for λ of W to be 110 (for example Pb^{+2} is 139[3]), the valence of W to be +6, and

Table 1 This table presents the total concentration of W (cumulative) in the cooling water loop at the time of the measurement in ppm. For comparison, representative isotope concentrations from the radioanalysis of the sample is also presented.

time hrs	W - stable $\mu\text{g/mL}$	W - 178 dpm/mL	Hf - 175 dpm/mL	Lu - 171 dpm/mL	theor resistivity ohm cm	corrosion rate mils/yr
0.25	0.54	2.68×10^5	1.09×10^5	1.45×10^5	4.57×10^5	36.1
1.75	1.0	5.68×10^5	2.62×10^5	4.29×10^5	2.47×10^5	9.6
3.25	2.2	1.40×10^6	7.66×10^5	1.54×10^6	1.12×10^5	11.3
6.25	6.7	4.73×10^6	2.79×10^6	5.33×10^6	3.68×10^4	17.9
22.75	34.0	2.02×10^7	1.26×10^7	1.74×10^7	7.25×10^3	25.0

the anion to be Cl^- . Figure 4 compares the calculated results with the solution resistivity measurements made during this time (from Table 1). As shown in this figure the theoretical calculations and experimental measurements agree well. The only exception is at 23 hrs. where

some deviation between the theoretical and experimental values is observed (approximately a factor of 4). It is somewhat surprising that the experimental resistivity data at 23 hrs. is greater than the theoretical value one would predict that the resistivity measurements would be sensitive to other impurities in the water loop (in addition to W^{+6} & X^{-6}). Thus, additional impurities would cause the experimental solution resistivity measurements to be lower than that calculated from the W concentration alone. The difference between the experimental data and theoretical data (from ICP) may also be explained if the solubility limit for W^{+4}/W^{+6} has been reached. In addition to dissolved solids, the ICP concentration analysis would also include any hydrated W-oxide which had precipitated from solution. Because the theoretical solution resistivities assume that all of the W measured by ICP is soluble W^{+6} , if any W^{+4}/W^{+6} had precipitated from solution this would result in an artificially low solution resistivity.

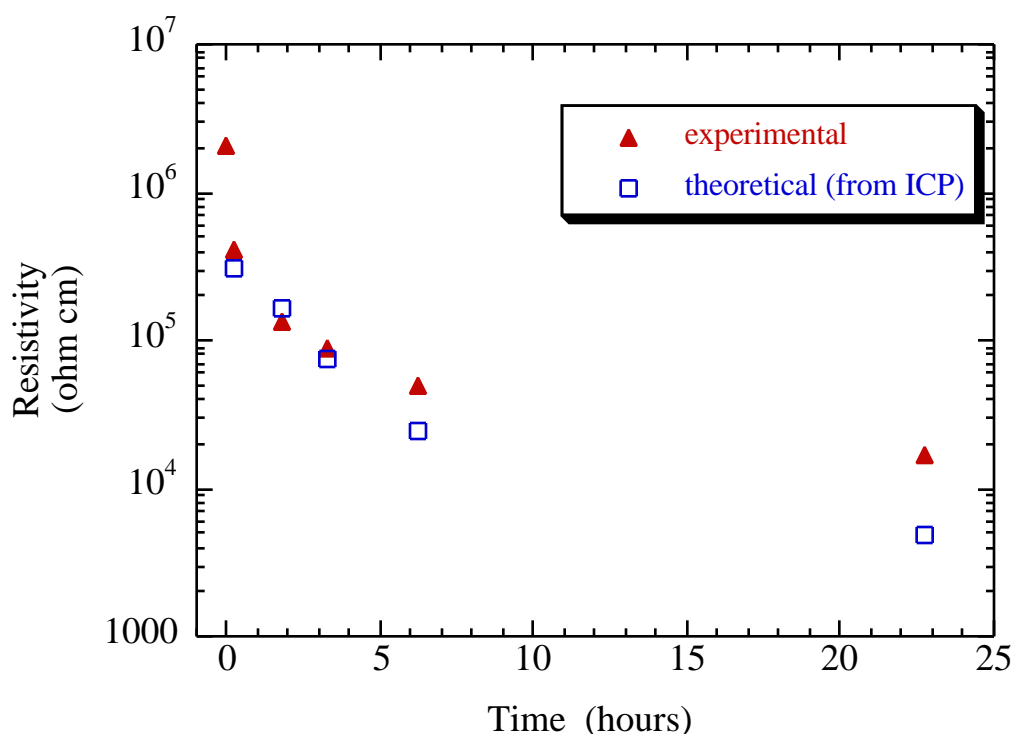


Figure 4 Measured resistivity during the final measurement period, Oct. 30-31, and the theoretical resistivity calculated from Equation 1 and the ICP analysis of water samples (Table 1).

Corrosion Rate Calculations From the ICP concentration analysis, it is also possible to calculate the corrosion rate of the tungsten target. Because we know the volume of the cooling water loop we can calculate the weight loss from the ICP concentrations. From the weight loss results we can calculate a corrosion rate (CR) from the relationship

$$CR = \frac{543m}{\rho A t} \quad \text{Eq. 2}$$

where **CR** is corrosion rate in mils/yr, **m** is weight loss (initial - final) in milligrams, **ρ** is density of W in grams/cm³, **A** is the exposed surface area of the W rod bundles in in², and **t** is time of exposure in hrs. Results of the corrosion rate calculations for the W target as a function of time are

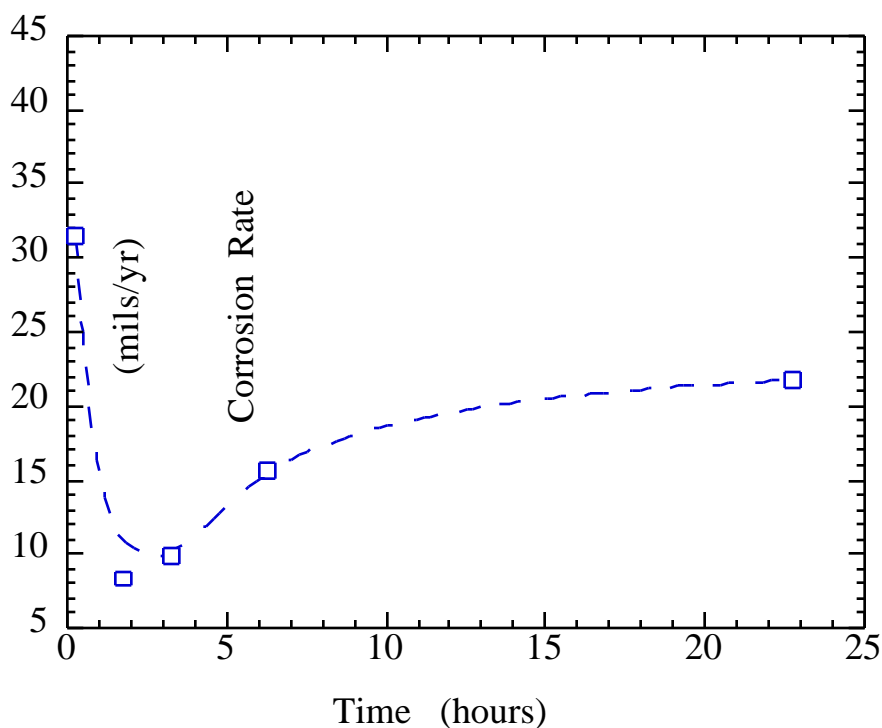


Figure 5 Corrosion rate of tungsten target as a function of time calculated from the ICP analysis of water samples taken during the final measurement period, Oct. 30-31, and Equation 2.

shown in Figure 5. As seen in this figure the corrosion rate when the beam initially goes on appears as the largest rate. This initial rate drops precipitously in the first 2 hours and then

gradually increases to what appears to be a steady state value of approximately 23 mils/yr (0.025"/yr). For a 1/8"-diameter tungsten rod (0.125" thick) a corrosion rate of 0.025" per year would result in a 50% decrease in the rod diameter in one year as it will be attacked circumferentially. It should be noted that these corrosion rate calculations assume uniform corrosion across the exposed tungsten surface area, and therefore, do not represent a conservative estimate as to the lifetime of the target. For example if the majority of dissolved W in the cooling water loop was from a small area around the beam spot, 10% of the sample area for example, the corrosion rates would be an order of magnitude higher. As a result a the corrosion rate would be closer 0.25" per year and, for a 1/8"-diameter tungsten rod (0.125" thick) a 100% decrease in the rod diameter would be observed in 3 months.

It has been demonstrated that the solution resistivity measurements agree well with those calculated from the concentration of W in the cooling water (Figure 4). Therefore, it may be possible to use resistivity measurements to estimate the corrosion rate of tungsten targets in a spallation neutron target / blanket cooling water system. Recognizing that the concentration of a monovalent anion (x^-) must be equal to 6 times that of the dissolved W^{+6} concentration, Equation 1 can be solved for C_{w+6} :

$$C_{w+6} = \frac{1}{\rho_m (\lambda_{w+6} + 6\lambda_{x-})} \quad \text{Eq. 3}$$

where C_{w+6} is the concentration of dissolved tungsten in moles/mL, λ is the respective equivalent conductance in $S \text{ cm}^2/\text{mol}$ ($S=(\text{ohm cm})^{-1}$) and, ρ_m is the measured solution resistivity in ohm cm. From C_{w+6} it is possible to determine the weight loss of W in milligrams (m in Equation 2):

$$m = C_{w+6} (184 \text{ g/mol}) V_{\text{sys}} \cdot 1000 \text{ mg/g} \quad \text{Eq. 4}$$

where V_{sys} is the volume of the water system in mL. From m and Equation 2 the corrosion rate of the W target can now be determined.

Figure 6 shows the corrosion rate of the W target as calculated from the solution resistivity measurements. For comparison the corrosion rates as calculated from the ICP concentration

analysis (Figure 4) are presented in this figure as well. While the corrosion rates at 23 hrs differ by a factor of 4, good agreement between the two separate methods for calculating corrosion rate is observed. Moreover, at times less than 6 hours the two methods agree within 25%. It may be noted in Figure 6 that at longer irradiation times the resistivity method for calculating corrosion rate underestimates that predicted from the ICP concentration analysis. As noted above (Figure 4) this is somewhat surprising as one would predict that the resistivity measurements would be sensitive to other impurities in the water loop (in addition to W^{+6} & X^{-6}). Thus, one would anticipate that the corrosion rates predicted by the resistivity measurements to be higher than those predicted by the ICP concentration analysis. As was the case in for the ICP corrosion rates (Figure 5) the corrosion rates calculated from solution resistivity measurements assume uniform corrosion. In all

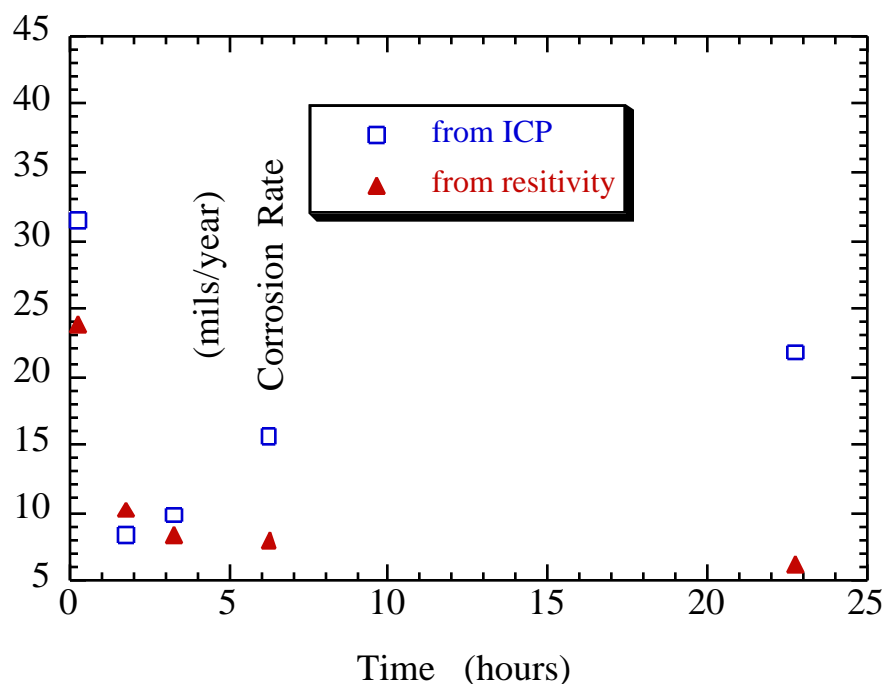


Figure 6 Corrosion rate calculations from solution resistivity measurements taken during the final measurement period, Oct. 30-31. For comparison the corrosion rates calculated from the ICP concentration analysis are also presented.

probability, this is not what is occurring in the system. Unfortunately, until a W specimen is removed from the cooling water loop and examined, the actual area will remain unknown.

Summary / Conclusions

Solution resistivity measurements of the tungsten cooling water loop at the LANSCE A6 target station found that the solution resistivity was proportional to beam current and time of irradiation. After flushing the system and refilling with deionized water and prior to turning the beam on, the solution resistivity was high (approximately 2 Mohm cm). After turning the beam on to 0.2 mA, the resistivity dropped by an order of magnitude (to approximately 0.5 Mohm cm). Ramping the beam current to 1 mA over 0.5 hours had little effect on the solution resistivity. However, over the next 12 hours of irradiation at 1 mA, the solution resistivity fell to approximately 0.07 Mohm cm. After this initial, exponential, decay the solution resistivity decreased linearly to a value of 0.001 Mohm cm.

ICP analysis of solution samples taken concurrently with resistivity measurements showed an increase in the concentration of W in the cooling water with beam current and time. These values were used to calculate theoretical solution resistivities as a function of time. These theoretical values agreed well with those observed experimentally.

From the solution resistivity measurements an estimate of the tungsten corrosion rates was calculated. These values were relatively close to those calculated from ICP concentrations, indicating that it is possible to use solution resistivity to estimate neutron spallation targets corrosion rates. To use resistivity measurements to estimate corrosion, however, several criteria must be met:

1. The water in the system must, initially, be distilled and deionized
2. The time of immersion from the last system flush / refill must be known
3. The relative corrosion rates of all other engineering materials exposed to the cooling water must be low relative to that of the spallation target
4. The volume of the system must be known
5. The area of the spallation target exposed to the cooling water must be known
6. The resistivity meter should be well calibrated

Provided that each criterion listed above is met, it should be possible to estimate the corrosion rate of a tungsten neutron spallation target using solution resistivity within an order of magnitude. Once again, it must be emphasized that whether the corrosion rate is determined from ICP concentration analysis or solution resistivity measurements each of these calculations assume uniform corrosion. If a localized area of corrosion the size of the beam spot is responsible for the majority of the W dissolution, then these true rates may be more than an order of magnitude higher than predicted.

It may also be noted that the corrosion rates measured in this work (from both ICP solution analysis and resistivity measurements) are undesirably high, suggesting that a corrosion mitigation strategy is essential to the successful operation of the future APT accelerator if unclad tungsten is to be used as the target material.

Reference

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